REMARKS

Applicants originally advanced the arguments below in a supplemental response dated on September 8, 2008 ("Supplemental Response") in reply to the Office Action dated June 6, 2008 ("Office Action") and Advisory Action dated August 18, 2008 ("Advisory Action"). The Examiner indicated in a telephone conference held on December 3, 2008 that he had never received the Supplemental Response and suggested that Applicants request continued examination (see below). To facilitate prosecution, Applicants respectfully comply. Co-filed with a Request for Continued Examination is the present document, Amendment under 37 cfr 1.114(D), which includes, in addition to the same amendments/arguments advanced in the Supplemental Response, additional claims and arguments for their patentability. Please disregard the previously filed Supplemental Response.

Applicants have amended claims 1 and 12 herein to correct typographical errors and introduced new claims 13-15. Support for the new claims can be found in the Specification at page 17, lines 3-7.

Upon entry of these new claims, claims 1-15 will be pending and under examination. It is respectfully requested that the Examiner reconsider this application in view of the following remarks.

Telephone interview summaries

During a telephone conference held on November 21, 2008, Applicants' council inquired about the Examiner's ruling in this case in view of the Supplemental Response. (Prior to this interview, Applicants' council e-mailed to the Examiner a letter, attached hereto as "Exhibit A," that summarized significant differences between the claimed method and those described in the cited prior art references.)The Examiner informed Applicants' council that, as he had yet to receive the Supplemental Response, he could not make a decision, but indicated that he would be willing to consider the arguments presented in the Supplemental Response upon receipt.

In a subsequent telephone conference held on November 26, 2008, Applicants' council found out that the Examiner still had not considered the arguments presented in the Supplemental Response. According to the Examiner, he had not done so as he still had not received the Supplemental Response.

In a third telephone conference held on December 1, 2008, the Examiner again informed Applicants' council that he had yet to receive the Supplemental Response.

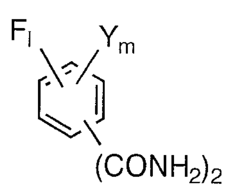
In yet another telephone conference held on December 3, 2008, Applicants' council informed the Examiner that, according to the USPTO website, the Supplemental Response was forwarded to him on September 30, 2008, expressed concern that the Supplemental Response had been misplaced, and offered to send the Examiner another copy. The Examiner suggested that Applicants file the Supplemental Response again along with a Request for Continued Examination.

<u>Rejection under 35 U.S.C. § 103</u>

Claims 1-12 are rejected as obvious over Masayoshi et al., European Patent Application No. 1275679 ("Masayoshi"), in view of Andrews et al., Aust. J. Chem., 1971, 412-422 ("Andrews"), and Hazen et al., U.S. Patent No. 5,011,997 ("Hazen"). See the Office Action, page 2, lines 10-16.

I

Independent claim 1 will be discussed first. This claim, as amended, covers a method for obtaining a fluorinated phenylenediamine of formula (2) shown below. The <u>diamine</u> of formula (2) is obtained via a Hoffman rearrangement by reacting a <u>diamide</u>, represented by formula (1) below, with NaOX, where X is either Br or Cl, in the presence of NaOH. In this method, the molar ratio of NaOH to diamide is in the range of <u>1.8-6.0</u>.



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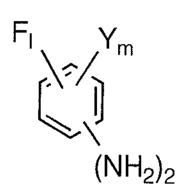

(2)

Applicants pointed out in their response dated August 5, 2008 ("First Response") that Masayoshi, the primary reference, teaches certain compounds of formula (2), but does not teach any method of making them from diamides.[1] Indeed, the Examiner concedes that "Masayoshi does not teach a method for the production of a fluorinated aromatic diamine from corresponding diamide." See the Office Action, page 3, last sentence. In other words, Masayoshi does not teach obtaining a diamine from its corresponding diamide, as required by claim 1, let alone using a molar ratio of NaOH to diamide in the range of 1.8-6.0, as also required by claim 1.

Applicants now turn to Andrews, a secondary reference. According to the Examiner, this reference discloses preparing an isophthalic-based diamine from a corresponding diamide with the Hoffmann rearrangement. The Examiner also states that Andrews teaches that the NaOH/diamide ratio is 2.25, which is within the range of claim 1. See the Office Action, page 4, lines 11-13.

Applicants pointed out in the First Response that Andrews discloses two methods which use the Hoffmann rearrangement for preparing an isophthalic-based diamine from its corresponding diamide. In the first method, the NaOH/diamide ratio was 2.25. This method resulted in a very low diamine yield of only **19%**. See page 416, lines 23-38. In the second method, characterized in Andrews as "a more efficient preparation" (see page 416, line 38), a NaOH/diamide ratio of about 1.56 was used, which resulted in a significantly increased diamine yield of **74%**. See page 416, lines 39-47.

In the First Response, Applicants calculated the NaOH/diamide ratio in the second to be about 1.56 as follows (based on three facts/assumptions, i.e., [i] 3.38 g of 2-

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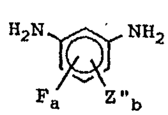
[1] As correctly pointed out by the Examiner, Mayoshi teaches "a fluorinated phenylenediamine of ... formula (6) where Z" denotes a chlorine, bromine or iodine ... *a* denotes fluorine atoms bonded to a benzene ring, representing an integer of 0-4 ... and *b* denotes the number of 'Z"' bonded to a benzene ring, representing 0-4 ... the total of *a* and *b* ought to be invariably 4." See the Office Action, page 2, line 17 through page 3, line 7, *a* and *b* have been italicized.



(6)

nitroisophthalic acid diamide and 100 mL of 1% aqueous NaOH solution was used,[2] [ii] the molecular weights of 2-nitroisophthalic acid diamide and NaOH are 211 g/mole and 40 g/mole, respectively, and [iii] the density of the 1% aqueous NaOH solution is identical to that of water, i.e.,1 g/ml):

Moles of NaOH = (100 ml x 1% x 1 g/ml)/40 g/mole = **0.025**;
Moles of diamide = 3.38 g diamide/211 g/mole = **0.016**;
NaOH/diamide ratio = **0.025/0.016** = 1.56.

Applicants also pointed out in the First Response that, given the significantly improved yield of the second (more efficient) method, using a NaOH/diamide ratio of about 1.56 (compared with the first (less efficient) method, using a NaOH/diamide ratio of about 2.25), a skilled artisan would have been motivated to decrease the NaOH/diamide ratio from 2.25 to 1.56, not increase it to a range of 1.8-6.0 as required by claim 1. Applicants concluded that Andrews clearly teaches away from using a NaOH/diamide ratio in the range of 1.8 to 6.0.

Having reviewed Applicants' arguments, the Examiner asserts in the Advisory Action that Andrews' more efficient method "produces less pure product (compare corresponding melting points of 141C and 145C). Therefore, in case where pure product is needed, method with higher NaOH/diamide ratio [i.e., the less efficient method] is preferred." See the Advisory Action, page 2, lines 3-4. Clearly, it is the Examiner's position that the melting point of 141°C, shown in Andrews' more efficient preparation, corresponds to a compound of lower purity.

Applicants respectfully submit that the Examiner's position is erroneous.[3] In Junino et al., US Patent No. 4,992,586, copy attached hereto as "Exhibit B," the melting point and elemental analysis of 2, 6-diaminonitrobenzene. See Exhibit B, column 8, lines 38-67. Note that 2, 6-diaminonitrobenzene taught in Exhibit B is the same compound as

[2] For the amount of diamide and the volume of 1% aqueous NaOH solution used in Andrew's second method, see page 416, lines 39 and 41, respectively.
[3] Applicants would like to point out that it is necessary to submit new evidence to address the Examiner's position that the melting point of 141°C corresponds to a compound of lower purity, a new ground raised in the Advisory Action, and have done so. It is respectfully requested that the new evidence and arguments set forth below based on it be considered.

1, 3-diamino-2-nitrobenzene taught in Andrews. For the Examiner's convenience, Applicants have reproduced the two relevant passages of Exhibit B below:

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_6H_7N_3O_2$	Found
C %	47.06	47.28
H %	4.57	4.58
N %	27.45	27.35
O %	20.91	20.80

Exhibit B discloses the above-shown elemental analysis data (i.e., calculated and experimentally determined) for 2, 6-diaminonitrobenzene having a molecular formula of $C_6H_7N_3O_2$. This data shows that (1) a compound with a molecular formula of $C_6H_7N_3O_2$ should have a C % of 47.1, a H% of 4.6, and a N% of 27.5, and (2) 2, 6-diaminonitrobenzene was found to have a C % of 47.3, a H% of 4.6, and a N% of 27.4.

Applicants would like to point out that Andrews also discloses elemental analysis data for this compound.[4] More specifically, 2, 6-diaminonitrobenzene, produced by Andrews' less efficient preparation, had a C% of 46.8, a H% of 4.6, and a N% of 27.1. See page 416, line 37.

Comparing the elemental analysis data of Exhibit B and Andrews with the calculated values for a 2, 6-diaminonitrobenzene having a molecular formula of $C_6H_7N_3O_2$ shown above, one can see that both the C% and N% data of Exhibit B are closer to the calculated values than the C% and N% data of Andrews. Indeed, the C% and N% data of Exhibit B only differ from the calculated values by 0.2 and 0.1, respectively, while the C% and N% data of Andrews differ by 0.3 and 0.4, respectively. It is well known in the art that the closer a compound's elemental analysis percentages

[4] Andrews discloses calculated C, H, and N percentage values for a $C_6H_7N_3O_2$ compound. However, these percentages are less accurate than those shown in Exhibit B, as Andrews' calculated percentage values have only 3 significant figures as opposed to 4 as in Exhibit B. Therefore, Applicants will not rely on Andrews' values. Note that the calculated values disclosed in Andrews are similar to those shown in Exhibit B.

are to its calculated percentages, the greater the compound's purity. Based on the elemental analysis data, it is clear that the 2, 6-diaminonitrobenzene described in Exhibit B has a higher purity than that prepared by Andrews' less efficient preparation.

The below-shown passage of Exhibit B demonstrates that 142°C is the melting point of the 2, 6-diaminonitrobenzene having higher purity. As mentioned above, 141°C is the melting point of the 2, 6-diaminonitrobenzene obtained by Andrews' more efficient preparation. Note that 145°C is the melting point of the 2, 6-diaminonitrobenzene obtained by Andrews' less efficient preparation. As the melting point of the compound obtained by Andrews' more efficient preparation is much closer than that of the compound described in Exhibit B, which has higher purity, it is clear that Andrews' more efficient preparation results in a 2, 6-diaminonitrobenzene having higher purity.

> Preparation of 2,6-diaminonitrobenzene
>
> 68 mg of palladium at a concentration of 10% on charcoal are added to 0.016 mole (3 g) of 4-chloro-2,6-diaminonitro-benzene in 6 ml of triethylamine, and 1.32 ml of formic acid are then added dropwise. A high exothermicity is noted. The reaction medium is heated to 90° C. for 1 hour 30. After dilution of the reaction mixture with ethanol, the catalyst is removed by hot filtration. The filtrate, evaporated to dryness under reduced pressure, enables a dry extract to be obtained. After dilution of the dry extract with water, the expected product precipitates. After filtration and washing with water, followed by drying under vacuum in the presence of phosphorus pentoxide, it is recrystallized from toluene. It melts at 142° C. (literature 141° C., 145° C.).

In sum, based on the elemental analysis and melting point data, Andrews' more efficient method produces a purer compound. Given this teaching, contrary to the Examiner's assertion, when a compound having high purity is needed, a skilled artisan would prefer Andrews' more efficient preparation using a NaOH/diamide ratio of about 1.56, not Andrews' less efficient preparation using a NaOH/diamide ratio of 2.25, which results in a product of lower purity and yield. In short, Applicants reiterate that Andrews teaches away from using a NaOH/diamide ratio in the range of 1.8 to 6.0.

Applicants now turn to Hazen, the other secondary reference. As discussed in Applicants Response, this reference discloses a method for producing a fluorinated aromatic diamine from its corresponding diamide. See the Abstract. As correctly pointed out by the Examiner, the Hoffmann rearrangement is "the same method used by both Hazen and the Application examined." See the Office Action, page 4, lines 6-8. The Examiner states in the Advisory Action that "since Hazen uses a diamine with much higher MW of diamine, in order to create certain pH, the amount of NaOH should be higher." See page 2, lines 5-7. Applicants would like to point out that the amount of NaOH required by a Hoffmann rearrangement depends on the molar quantity of diamide, not on the molecular weight of a diamine.[5]

Applicants would also like to point out that nowhere in Hazen does it mention using a NaOH/diamide ratio in the range of 1.8 to 6.0. Clearly, Hazen does not suggest a yield/purity trend as a function of NaOH/diamide ratio, let alone a NaOH/diamide ratio in the range of 1.8 to 6.0, as required by amended claim 1.

To conclude, Masayoshi does not teach using a NaOH/diamide ratio of 1.8 to 6.0 in producing a diamine from a diamide, as required in the method claim 1, and neither Andrews nor Hazen cures this deficiency. Thus, the combination of these three references does not render claim 1 obvious. Nor does their combination render obvious claims 2-4 and 7-10, all of which depend, directly or indirectly, from claim 1. Clearly

Applicants now turn to the rejection of independent claims 5, 6, 11, and 12. Claims 5 and 11 each cover a method for obtaining a polyamic acid while claims 6 and 12 each cover a method for obtaining a polyimide. The first step in each method is identical to that of claim 1, which is discussed above. Thus, for the same reasons and facts set forth above, claims 5, 6, 11, and 12 are also not rendered obvious by the combination of Masayoshi, Andrews, and Hazen.

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[5] Indeed, claim 1 defines NaOX/diamide and NaOH/diamide as molar ratios, i.e., dependent on the molar quantity of diamide (not diamine), NaOX, and NaOH.

II

Even if the Examiner had established a prima facie case of obviousness (which Applicants do not concede) in view of the combination of Masayoshi, Andrews, and Hazen, it could be successfully rebutted by a showing of unexpected results.

As discussed below, Applicants' use of a multi-halogenated phenylenediamide leads to unexpected results. In Applicants' method, the diamide is reacted with NaOX and NaOH in a Hoffmann rearrangement reaction to produce a corresponding diamine in high yield. As shown in Examples 1 and 3 of the Specification, the yield of diamide obtained by the Hoffmann rearrangement reaction was 90.7% and 88.5%, respectively.[6]

The Hazen method uses a multi-halogenated biphenylenediamide. This diamide is reacted with NaOX and NaOH in a Hoffmann rearrangement reaction to produce a corresponding diamide. During the reaction, Hazen's diamide generates large quantities of azo by-products, resulting in a diamine yield of about 60-80%.[7] See column 3, lines 20-21, and column 4, line 67. Indeed, according to Hazen, "[t]he first step of the process known as the Hoffmann Reaction for the conversion of an amide to the primary amine ... does not produce a high purity product in high yield but rather a low purity product which is extremely difficult to purify." See column 2, lines 3-8.

The two Andrews methods both use a NO_2-containing phenylenediamide. This diamide is reacted with NaOX and NaOH in a Hoffmann rearrangement reaction to produce a corresponding diamide. In both methods, the yield of diamine produced was low, i.e., 19% and 74%. See page 416, lines 36 and 47.

As can be seen from the comparison of Applicants' method with those of Hazen and Andrews, the use of Applicants' multi-halogenated phenylenediamide in the

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[6] These yields were calculated from the dried solid isolated before purification as follows: [(weight of crude diamine collected / molecular weight of diamine)/(moles of diamide initially used)] x 100%. For Examples 1 and 3 of the Specification (pages 23-24 and 25-26), the calculations are as follows:
Example 1:[(11.60/180.10g)/(0.071moles)] x 100%] = 90.7%
Example 3 :[(10.61/196.56g)/(0.061moles)] x 100%] = 88.5%.

[7] The Examiner asserts that "Hazen teaches [that] the Hoffmann rearrangement process results in a product [in] high yield." See the Office Action, page 6, lines 1-2. Applicants would like to point out that to obtain a high yield Hazen relies on a subsequent reduction step to convert the azo by-product into a diamine. This essential second step to the Hazen method CANNOT be considered part of the Hoffmann rearrangement reaction. Indeed, it is a completely separate reaction. Thus, the yields shown are those before purification using this separate reaction.

Hoffmann rearrangement reaction resulted in unexpectedly higher yields. Applicants would also like to point out that neither Hazen nor Andrews suggests the use of these diamides, let alone that their use will lead to higher diamine yields.

For the reasons and facts discussed above, Applicants submit that using a multi-halogenated phenylenediamide results in a significant and unexpected improvement in yield for diamines obtained via a Hoffmann rearrangement reaction.

New Claims

Claims 13-15 have been added to cover particular embodiments of this invention. These new claims dependent from claims 1, 5, and 6, respectively. For the same reasons set forth above, they are patentable over Masayoshi, Andrews, and Hazen, either alone or in combination.

CONCLUSION

It is believed that all of the pending claims have been addressed. However, the absence of a reply to a specific rejection, issue or comment does not signify agreement with or concession of that rejection, issue or comment.

In addition, because the arguments made above may not be exhaustive, there may be reasons for patentability of any or all pending claims (or other claims) that have not been expressed.

Finally, nothing in this paper should be construed as an intent to concede any issue with regard to any claim, except as specifically stated in this paper, and the amendment of any claim does not necessarily signify concession of unpatentability of the claim prior to its amendment.

The Request for Continued Examination fee in the amount of $ 810 and the Petition for Extension of Time fee in the amount of $ 1110 is being paid concurrently herewith on the Electronic Filing System (EFS) by way of Deposit Account authorization.

Please apply any other charges or credits to Deposit Account No. 50-4189, referencing Attorney Docket No. 60004-109US1.

Respectfully submitted,

Date: 12-8-08

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EXHIBIT A

OCCHIUTI ROHLICEK & TSAO LLP

PATENT LAW

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November 20, 2008

Examiner Gregory Listvoyb
U.S. Patent & Trademark Office
Commissioner for Patents
Washington, D.C. 20231

Re.:	Method for Production of Fluorinated Phenylenediamine
Application No.:	10/561,048
Our Ref.:	60004-109US1

Dear Examiner Listvoyb:

Thank you for granting a telephone interview, scheduled for November 21, 2008 at 1:00 pm, to discuss the above-referenced application.

We summarize our supplementary response below to facilitate our discussion. This supplementary response address two issues raised in the advisory action.

Issue (I): Andrews

You asserted the diamide produced by a method disclosd in Andrews has a higher purity. According to this method, the Andrews diamine has a yield of 19% and a melting point of 145°C.

In our supplementary response, we presented data disclosed in U.S. Patent No. 4,992,586 showing that a m.p. 142°C correspond to a purer diamine. See pages 11-14. In view of this data, we reiterated that the Andrews amide having a m.p.of 145°C, instead of 142°C, is less pure. We would also like to point out that our method produces very different diamines having a purity of at least 99.8 % and a yield greater than 63% (already pointed out in our response to the first office action). In short, the Andrews method and ours are very different.

Issue (II): Hazen

You restated your position that as Hazen uses a diamide with a much higher molecular weight, a higher amount of NaOH would be needed to create the certain pH, i.e., an NaOH/diamide ratio > 6.0. However, your position is not accurate. It is the number of amide groups that determines the amount of NaOH needed, not the molecular weight of the diamide. You also did not provide a reason why a skilled artisan would lower the NaOH amount so that the NaOH/diamide ratio would be in our recited range of 1.8 to 6.0.

We would like to point out that Hazen discloses that the Hoffmann rearrangement does not produce a high purity product in high yield. Rather it produces a low purity product which is extremely difficult to purify. See column 2, lines 4-8.

Nowhere does Hazen suggest that NaOH/diamide ratio in the range of 1.8 to 6.0 would result in a higher purity diamine or an increase in diamine yield.

We look forward to discussing with you our above remarks.

Sincerely yours,

Y. Rocky Tsao

Y. Rocky Tsao, Ph.D., J.D.
Attorney for Applicants
Reg. No. 34,053

TELEPHONE: (617) 500-2503
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EXHIBIT B

United States Patent [19]

Junino et al.

[11] **Patent Number: 4,992,586**

[45] **Date of Patent: Feb. 12, 1991**

[54] **PROCESS FOR PREPARING 2-NITRO-META-PHENYLENEDIAMINES**

[75] Inventors: **Alex Junino**, Livry-Gargan; **Gerard Lang**, Saint-Gratien; **Nicole Jehanno**, Brunoy; **Jean J. Vandenbosche**, Aulnay-sous-Bois, all of France

[73] Assignee: **L'Oreal**, Paris, France

[21] Appl. No.: **253,594**

[22] Filed: **Oct. 5, 1988**

Related U.S. Application Data

[62] Division of Ser. No. 15,032, Feb. 17, 1987, Pat. No. 4,797,129.

[30] **Foreign Application Priority Data**

Feb. 14, 1987 [LU] Luxembourg 86308

[51] **Int. Cl.**[5] **C07C 211/00**

[52] **U.S. Cl.** **564/367**; 564/368; 564/369; 564/371; 564/441

[58] **Field of Search** 564/406, 412, 441, 367

[56] **References Cited**

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3,586,725	6/1971	Hunter	564/406 X
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OTHER PUBLICATIONS

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Loudon, "Chemical Abstracts", vol. 35, pp. 1774 (1941).

Andrews, "Chemical Abstracts", vol. 74, p. 257, Section No. 6364h (1971).

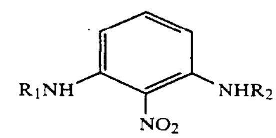
Primary Examiner—Robert V. Hines

Attorney, Agent, or Firm—Cushman, Darby & Cushman

[57] **ABSTRACT**

A dye composition for keratinous fibers comprising a solvent and at least one dye which is a compound of formula:

(I)



in which R_1 and R_2 are each, independently of each other, hydrogen, an alkyl group, a mono- or polyhydroxylated alkyl group, an alkyl group susbsituted by an alkoxy or hydroxyalkoxy group, or an aminoalkyl group, the amino group of which is optionally substituted with one or two alkyl or hydroxyalkyl groups, and it being possible for the nitrogen atom also to form part of a heterocyclic ring, all the abovementioned alkyl groups or moieties containing from 1 to 6 carbon atoms, or, if the compound of formula (I) contains an amino group which can be salified, a cosmetically acceptable salt thereof.

7 Claims, No Drawings

PROCESS FOR PREPARING 2-NITRO-META-PHENYLENEDIAMINES

This is a division of application Ser. No. 015,032, filed Feb. 17, 1987, patent No. 4,797,129.

The present invention relates to a dye composition for keratinous fibres based on 2-nitro-meta-phenylenediamines, to a process for dyeing keratinous fibres, especially human hair, using the dye composition, to a process for the preparation of these compounds, and to certain 2-nitro-meta-phenylenediamines employed.

It is known that nitro derivatives of the benzene series can be used to impart a direct coloration, or additional highlights in the case of oxidation dyeing, to keratinous fibres, especially to human hair.

The use, in direct dyeing, of 4-nitro-meta-phenylenediamines, which are yellow dyes, has already been proposed in French Pat. Nos. 1,508,405 and 1,584,965.

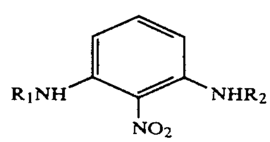
It is important, for colored highlights, to be able to produce warm shades such as copper, mahogany or red.

We have surprisingly found that 2-nitro-meta-phenylenediamines which, contrary to all expectations, are red to orange-red dyes, can be used to impart orange-red to red shades, which are useful warm shades, to keratinous fibres.

The dyes exhibit good solubility in the cosmetic media which are conventionally employed in hair dyeing and have the advantage of keeping well in the substrates which are usually employed in oxidation-dyeing compositions, especially in a reducing alkaline medium. This enables them to be combined with precursors of oxidation dyes to produce shades which are rich in highlights.

The present invention therefore provides a dye composition for keratinous fibres comprising a solvent and a tinctorially effective amount of at least one dye which is a compound of formula:

(I)



in which R_1 and R_2 are each, independently of each other, hydrogen, an alkyl group, a mono- or polyhydroxylated alkyl group, an alkyl group substituted by an alkoxy or hydroxyalkoxy group or an aminoalkyl group, the amino group of which is optionally substituted with one or two alkyl or hydroxyalkyl groups, and it being possible for the nitrogen atom of the aminoalkyl group to form part of a heterocyclic ring, all the abovementioned alkyl groups or moieties containing from 1 to 6 carbon atoms or, if the compound of formula (I) contains an amino group which can be salified, a cosmetically acceptable salt thereof.

Preferred alkyl groups or moieties have from 1 to 4 carbon atoms.

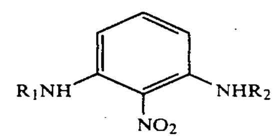
Preferred R_1 and R_2 groups are hydrogen and methyl, ethyl, n-propyl, n-butyl, β-hydroxyethyl, γ-hydroxypropyl, β-hydroxypropyl, β, γ-dihydroxypropyl, methoxyethyl, ethoxyethyl, β-hydroxyethoxyethyl, β-aminoethyl, β-hydroxyethylaminoethyl and β-diethylaminoethyl groups.

Compounds of formula (I) which are preferably employed in the dye composition of the invention include:

2,6-diaminonitrobenzene
2-(β-hydroxyethyl)amino-6-(β-hydroxyethyl)aminonitrobenzane
2-amino-6-methylaminonitrobenzene
2-amino-6-(β-hydroxyethyl)aminonitrobenzene
2-(γ-hydroxypropyl)amino-6-(γ-hydroxypropyl-)aminonitrobenzene
2-(β-hydroxyethoxyethyl)amino-6-(β-hydroxyethoxyethyl)aminonitrobenzene
2-(β,γ-dihydroxypropyl)amino-6-(β, γ-dihydroxypropyl)aminonitrobenzene
2-(β-hydroxypropyl)amino-6-(β-hydroxypropyl-)aminonitrobenzene
2-(β-methoxyethyl)amino-6-(β-methoxyethyl)aminonitrobenzene
2-(β-diethylaminoethyl)amino-6-(β-diethylaminoethyl)-aminonitrobenzene, and
2-(β-aminoethyl)amino-6-(β-aminoethyl)aminonitrobenzene.

The present invention also provides compounds of formula (I):

(I)



in which R_1 and R_2 have the abovementioned meanings provided that they are not simultaneously hydrogen.

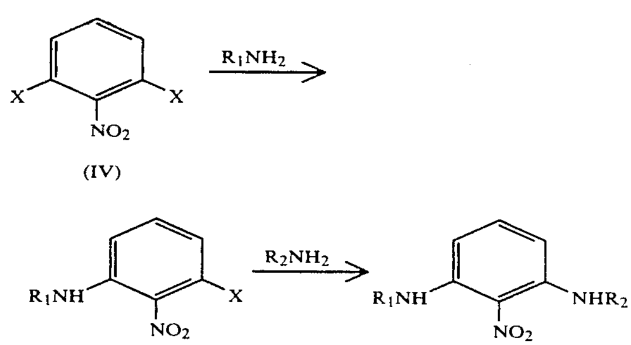
The present invention also proves processes for preparing the compounds of formula (I).

The compounds of formula (I) may be prepared according to any one of three processes:

1st process:

This can only be applied to the preparation of compounds of formula (I) in which R_2 is other than hydrogen.

In a first step, a 2,6-dihalonitrobenzene of formula (IV) is reacted with an amine of formula R_1NH_2 or ammonia to produce a compound of formula (III) in which R_1 has the same meaning as above; the compound of formula (III) is then reacted with an amine of formula R_2NH_2, wherein R_2 has the same meaning as above, except for hydrogen, to produce a compound of formula (I) according to the following reaction scheme:



(IV) (III) (I)

wherein R_1 and R_2 have the meanings indicated above and X is a halogen, preferably chlorine. Compounds of formula (I) in which R_2 is identical to R_1 can be produced directly by the action of an amine of formula NH_2R_1, wherein R_1 has the above meaning, except for hydrogen, on the compound of formula (IV).

The substitution of the halo groups by the amino groups NHR_1 and NHR_2 can be performed in the absence or presence of a solvent. Solvents which are generally employed include lower alcohols, dimethylformamide, dimethyl sulphoxide, N-methylpyrrolidone and N,N'-dimethyl-propyleneurea. In the case where ammonia or the amines NH_2R_1 or NH_2R_2 are employed in aqueous solution, it is preferable, for solubility reasons, to add a third solvent chosen from those mentioned above.

The reaction temperature is generally from 10° C. to the reflux temperature of aqueous ammonia, the amine NH_2R_1 and/or NH_2R_2, the solvent or the reaction mixture. The reaction temperature is preferably from 20° C. 170° C.

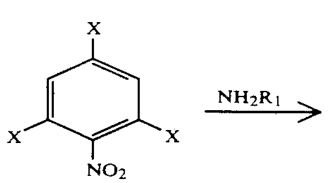
In the case of amines NH_2R_1 and/or NH_2R_2 having a boiling temperature lower than or equal to ambient temperature, or gaseous ammonia, the substitution may be performed in an autoclave, a pressure of 25 kg/cm^2 being generally sufficient.

Compounds of formula (III) in which R_1 is hydrogen, alkyl or hydroxyalkyl and X is chlorine can be prepared by reacting 2,6-dichloronitrobenzene and ammonia or the corresponding amine NH_2R_1 (see Beilstein, vol.12 p. 1648; JACS 61 (1939) p. 2658; JACS 64 (1942) p. 1285 and J. Org. Chem. vol. 42, No. 1, (1977) p. 166).

2,6-dihalonitrobenzenes can be prepared according to the processes which are described in the literature: for example, 2,6-dichloronitrobenzene may be prepared by oxidation of 2,6-dichloroanline either with trifluoroperacetic acid, according to Organic Syntheses vol. 49, page 47, or with a solution of sodium perborate in acetic acid, according to Alexander McKillop and Jonathan A. Tarbin, Tetrahedron Letters, vol. 24, No. 14, pages 1505–1508 (1983).

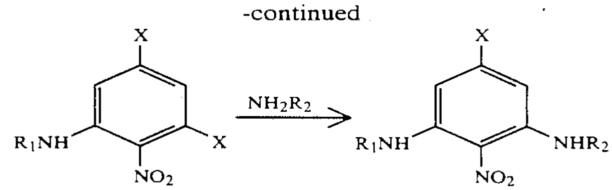
Second process:

The compounds of formula (I) may be prepared from a 2,4,6-trihalonitrobenzene of formula (VI) which, in a first step, is reacted with an amine of formula NH_2R_1, wherein R_1 has the meaning specified above, or with ammonia, to produce a compound of formula (V) which, in a second step, is reacted with an amine of formula NH_2R_2 wherein R_2 is as defined above or ammonia to produce a compound of formula (II) in accordance with the following reaction scheme:



(VI)

-continued



(V) (II)

wherein R_1, R_2 and X have the meanings indicated above.

The compounds of formula (II) in which the group R_2 is identical with the group R_1 can be prepared in a single step from the compounds of formula (VI). The synthesis of 2,6-diamino-4-chloro-nitrobenzene by the reaction of ammonia with 2,4,6-trichloronitrobenzene is known (Beilstein, vol. 13, p.58).

The reaction conditions are similar to those described in the first process above. When the halogen is chlorine, simultaneous substitution of the chlorine by the NHR_1 group generally requires a shorter time and a lower temperature in the case of the compound of formula (VI) than in the case of the compound of formula (IV).

The compounds of formula (I) can be obtained by dehalogenation of the compounds (II), which dehalogenation may advantageously be carried out with the aid of triethylamine formate in the presence of palladium on charcoal, as described by N.A. Cortese and R.F. Heck in J. Org, Chem. vol. 42, No. 22, page 3491 (1977), or by any other method which does not involve the simultaneous reduction of the nitro group.

We have found that the dehalogenation reaction can be performed in the presence of a solvent such as an alcohol, dimethylformamide, N-methylpyrrolidone or acetic acid.

Palladium may be employed on a support such as barium sulphate, barium carbonate, alumina or calcium carbonate.

We have found it especially advantageous to use a palladium catalyst on calcium or barium carbonate in the presence of acetic acid, formic acid and triethylamine.

The compounds produced using this method are of greater purity than those produced by the method described in J. Org. Chem., vol. 42, No. 22, page 3491 (1977).

The 2,4,6-trihalonitrobenzenes can be prepared according to the methods described in the literature: for example, 2,4,6-trichloronitrobenzene may be prepared by oxidation of 2,4,6-trichloroaniline either with trifluoro-peracetic acid, according to Organic Syntheses Vol. 49, page 47, or with a solution of sodium perborate in acetic acid, according to Alexander McKillop and Jonathan A. Tarbin, Tetrahedron Letters, Vol. 24, No. 14, page 1505–1508 (1983).

The compound of formula (I) in which R_1 and R_2 are both hydrogen may also be prepared from 2-nitroisophthalic acid according to the process described in J.C.S. Perkin Trans. 2 (3), page 590, (1981).

Third process:

2,6-diaminonitrobenzene is subjected to conventional chemical alkylation, hydroxyalkylation or aminoalkylation to produce a compound of formula (I) in which R_1 and/or R_2 are other than hydrogen. These alkylation, hydroxyalkylation or aminoalkylation processes are

described, for example, in French Pat. Nos. 2,348,911, 2,497,662 and 2,492,370.

The compounds of formula (I) which are more particularly preferred according to the present invention are:

2-(β-hydroxyethyl)amino-6-(β-hydroxyethyl)aminonitro-benzene,

2-amino-6-methylaminonitrobenzene,

2-amino-6-(β-hydroxyethyl)aminonitrobenzene

2-(γ-hydroxypropyl)amino-6-(γ-hydroxypropyl)amino-nitrobenzene,

2-(β-hydroxyethoxyethyl)amino-6-(β-hydroxyethoxyethyl)-aminonitrobenzene,

2-(β,γ-dihydroxypropyl)amino-6-(β,γ-dihydroxy-propyl)-aminonitrobenzene,

2-(β-hydroxypropyl)amino-6-(β-hydroxypropyl-)amino-nitrobenzene,

2-(β-methoxyethyl)amino-6-(β-methoxyethyl)aminonitro-benzene,

2-(β-diethylaminoethyl)amino-6-(β-diethylaminoethyl)-aminonitrobenzene, and

2-(β-aminoethyl)amino-6-(β-aminoethyl)aminonitro-benzene.

The dye compositions according to the present invention generally contain the compounds of formula (I) in a proportion of from 0.001 to 5% by weight, preferably from 0.05 to 2% by weight, relative to the total weight of the composition.

The solvent is preferably a cosmetic vehicle comprising water, but it is also possible to add organic solvents to the compositions in order to dissolve compounds which might not be sufficiently soluble in water. Examples of such solvents are lower alkanols (e.g. containing up to 6 or up to 4 carbon atoms) such as ethanol and isopropanol, aromatic alcohols such as benzyl alcohol or phenoxyethanol, polyols such as glycerol and glycols and glycol ethers such as 2-butoxyethanol or 2-ethoxyethanol, ethylene glycol, propylene glycol, diethylene glycol monomethyl ether and monoethyl ether. These solvents are preferably present in a proportion of from 1 to 75% by weight, particularly from 5 to 50% by weight, relative to the total weight of the composition.

The compositions may contain anionic, cationic, nonionic or amphoteric surface-active agents or mixtures thereof. These surface-active products are generally present in the compositions of the invention in a proportion of from 0.5 to 55% by weight, preferably from 4 to 40% by weight, relative to the total weight of the composition.

The compositions may be thickened, preferably with sodium alginate, gum arabic, xanthane gum, cellulose derivatives such as methylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose or carboxymethylcellulose, or a polymer which acts as a thickener such as an acrylic acid derivative. Inorganic thickening agents such as bentonite can also be used. These thickening agents are preferably present in a proportion of from 0.1 to 10% by weight, particularly from 0.5 to 2% by weight, relative to the total weight of the composition.

The compositions according to the invention may also contain various adjuvants commonly employed in hairdyeing compositions, and in particular penetrating agents, dispersing agents, sequestering agents, film-forming agents, buffers and/or perfumes.

These compositions may be presented in various forms such as liquids, creams, gels or any other appropriate form for performing hair dyeing. They may be packaged with a propellent agent in aerosol bottles.

The pH of the dye compositions is generally from 3 to 11.5, preferably from 5 to 11.5. It can be adjusted to the required value with an alkalizing agent such as aqueous ammonia, sodium, potassium or ammonium carbonate, sodium or potassium hydroxide, an alkanolamine such as mono-, di- or triethanolamine, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol, or an alkylamine such as ethylamine or triethylamine, or with an acidifying agent such as phosphoric, hydrochloric, tartaric, acetic, lactic or citric acid.

When the compositions are intended to be used in a direct hair-dyeing process, they may additionally contain at least one direct dye other than that of formula (I) or a salt thereof, such as an azo or anthraquinone dye, for example 1,4,5,8-tetraaminoanthraquinone, an indophenol, an indoaniline or a nitro dye of the benzene series.

The concentration of the direct dyes is generally from 0.001 to 5% by weight relative to the total weight of the composition.

The present invention also provides a method of dyeing keratinous fibres, especially human hair, wherein a dyeing composition as defined above is applied to the fibres.

The compositions can be used in a direct dyeing process and can, for example, be applied to the keratinous fibres for from 5 to 50 minutes, and the fibres are rinsed, washed if desired optionally using a shampoo, rinsed again and dried.

The compositions according to the present invention may also be used in the form of hairsetting lotions intended to impart a slight coloration or highlights to the hair and to improve the set retention. In this case, they are generally in the form of aqueous, alcoholic or aqueous alcoholic solutions containing at least one cosmetic resin and they can be applied to previously washed and rinsed damp hair which, if desired, is wound on rollers and is then dried.

Examples of cosmetic resins include polyvinylpyrrolidone, crotonic acid-vinyl acetate or vinylpyrrolidone-vinyl acetate copolymers, copolymers of half-esters of maleic anhydride with butyl vinyl ether or of maleic anhydride with methyl vinyl ether, copolymers of maleic acid with methyl or butyl vinyl ethers, as well as any other cationic, anionic, nonionic or amphoteric polymer usually employed in a composition of this type. These cosmetic resins generally are present in a proportion of from 0.1 to 4% by weight, preferably from 0.5 to 3% by weight, based on the total weight of the composition.

When the compositions according to the invention form oxidation dye compositions involving development with an oxidizing agent, the compounds of formula (I) are intended to impart highlights to the final dye.

Thus the dye composition comprising a solvent and at least one compound of formula (I) or a salt thereof can be used in the direct dyeing of keratinous fibres or for the oxidation dyeing of these fibres, in which case the compounds of formula (I) impart additional highlights to the basic color obtained by oxidizing development of the oxidation dye precursors.

These compositions contain precursors of oxidation dyes in combination with at least one nitro dye of formula (I) and, if desired, other direct dyes.

They may, for example, contain para-phenylenediamines such as para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,6-dimethyl-

paraphenylenediamine, 2,6-dimethyl-3-methoxy-paraphenylenediamine, N-(β-methoxyethyl)-paraphenylenediamine, N, N-(β-hydroxyethyl)-paraphenylenediamine N-(ethyl,carbamylmethyl)-4-aminoaniline or salts thereof.

They may also contain para-aminophenols, for example para-aminophenol, N-methyl-para-aminophenol, 2-chloro-4-aminophenol, 3-chloro-4-aminophenol, 2-methyl-4-aminophenol, or their salts or ortho-aminophenol.

They may also contain heterocyclic derivatives such as 2,5-diaminopyridine or 7-aminobenzomorpholine.

The compositions may contain, in combination with the precursors of oxidation dyes, couplers which are well known in the state of the art.

Examples of such couplers include meta-diphenols, meta-aminophenols and their salts, meta-phenylenediamines and their salts, meta-acylaminophenols, meta-ureidophenols, meta-carbalkoxyaminophenols, α-naphthol, couplers containing an active methylene group, such as diketone compounds and pyrazolones and heterocyclic couplers derived from pyridine and from benzomorpholine.

In addition these compositions may contain a reducing agent, which is generally present in a proportion of from 0.05 to 3% by weight relative to the total weight of the composition.

The oxidation dye precursors are preferably employed in the compositions of the invention in a concentration of from 0.001 to 5% by weight, more preferably from 0.03 to 2% by weight, based on the total weight of the composition. The couplers are preferably present in a proportion of from 0.001 to 5% by weight, more preferably from 0.015 to 2% by weight. The pH of the oxidation dye compositions is preferably from 7 to 11.5 and may be adjusted with an alkalizing agent as defined above.

The process of dyeing keratinous fibres, especially human hair, employing development by means of an oxidizing agent, consists in applying to the hair a dye composition according to the invention. The development of the color may then take place slowly in the presence of atmospheric oxygen, but preferably a chemical development system is used. In most cases it is hydrogen peroxide, urea peroxide or a persalt. In particular, a 20-volume hydrogen peroxide solution can be used.

Once the composition containing the oxidizing agent has been applied to the keratinous fibres, it is left in place for from 10 to 50 minutes, preferably from 15 to 30 minutes, after which the keratinous fibres are rinsed, washed with a shampoo if desired and are rinsed again and dried.

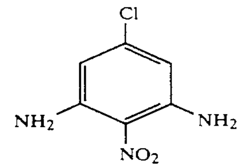
The examples which follow further illustrate the present invention.

REFERENCE EXAMPLE

Preparation of 2,6-diaminonitrobenzene

First step

Preparation of 4-chloro-2,6-diaminonitrobenzene



0.34 mole (76 g) of 2,4,6-trichloronitrobenzene is added, in an autoclave, to 400 ml of 28% strength aqueous ammonia in water and 100 ml of ethanol. The reaction mixture is heated for 16 hours at 155°-160° C., the pressure being 20 kg/cm^2. The expected product precipitates after cooling. After filtration and reslurrying in water until the aqueous washes are neutral, it is dried in vacuum in the presence of phosphorus pentoxide. After recrystallization from isopropanol, in order to remove a gum, it melts at 202° C. (literature 192 °-194° C).

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_6H_6ClN_3O_2$	Found
C %	38.40	38.55
H %	3.20	3.26
N %	22.40	22.43
O %	17.06	16.88
Cl %	18.93	18.74

Second step

Preparation of 2,6-diaminonitrobenzene

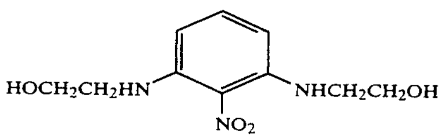
68 mg of palladium at a concentration of 10% on charcoal are added to 0.016 mole (3 g) of 4-chloro-2,6-diaminonitro-benzene in 6 ml of triethylamine, and 1.32 ml of formic acid are then added dropwise. A high exothermicity is noted. The reaction medium is heated to 90° C. for 1 hour 30. After dilution of the reaction mixture with ethanol, the catalyst is removed by hot filtration. The filtrate, evaporated to dryness under reduced pressure, enables a dry extract to be obtained. After dilution of the dry extract with water, the expected product precipitates. After filtration and washing with water, followed by drying under vacuum in the presence of phosphorus pentoxide, it is recrystallized from toluene. It melts at 142° C. (literature 141° C., 145° C.).

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_6H_7N_3O_2$	Found
C %	47.06	47.28
H %	4.57	4.58
N %	27.45	27.35
O %	20.91	20.80

EXAMPLE 1

Preparation of 2-(β-hydroxyethyl)amino-6-(β-hydroxyethyl)aminonitrobenzene (Second process)



First step

Preparation of 4-chloro-2-(β-hydroxyethyl)amino-6-(β-hydroxyethyl)aminonitrobenzene

0.132 mole (30 g) of 2,4,6-trichloronitrobenzene is heated to 95° C. in 120 ml of ethanolamine. After 30 minutes, the reaction mixture is poured onto 240 g of a mixture of ice and water. The expected product precipitates. It is filtered off, washed with water and then dried under vacuum in the presence of phosphorus pentoxide. After recrystallization from absolute ethanol, it melts at 154° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{10}H_{14}ClN_3O_4$	Found
C %	43.56	43.37
H %	5.08	5.11
N %	15.24	15.25
O %	23.23	23.45
Cl %	12.88	13.01

Second step

Preparation of 2-(β-hydroxyethyl)amino-6-β-hydroxyethyl)aminonitrobenzene

354 mg of palladium at a concentration of 10% on charcoal are added to 0.084 mole (23.1 g) of 4-chloro-2-(β-hydroxyethyl)amino-6-(β-hydroxyethyl)aminonitrobenzene in 23.7 g of triethylamine. 7 ml of formic acid are then run in dropwise. A high exothermicity is noted. The reaction mixture is heated to 70° C. for 1 hour 30. After dilution of the reaction mixture with ethanol, the catalyst is removed by hot filtration. The filtrate, evaporated to dryness under reduced pressure, enables a dry extract to be obtained. After dilution of the dry extract with water, the expected product precipitates. After being filtered off, washed with water and then dried under vacuum in the presence of phosphorus pentoxide, it is recrystallized twice from isopropanol. It melts at 103°-104° C., resolidifies and then melts at 112°-113° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{10}H_{15}N_3O_4$	Found
C %	49.78	49.66
H %	6.27	6.28
N %	17.42	17.40
O %	26.53	26.46

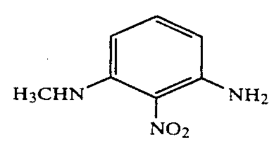
EXAMPLE 2

Preparation of 2-(β-hydroxyethyl)amino-6-(β-hydroxyethyl)aminonitrobenzene (First process)

0.25 mole (48 g) of 2,6-dichloronitrobenzene, prepared according to the method described by Alexander McKillop and Jonathan A. Tarbin in Tetrahedron Letters, Vol. 24 No. 14, page 1505 (1983), is added to 200 ml of ethanolamine. The mixture is heated to 98° C. for 8 hours. The reaction mixture is poured onto ice. After phase separation, the precipitate is taken up in the minimum quantity of ethanol, with stirring. After dilution with a mixture of ice and water, the expected product is filtered off, washed with water and then recrystallized from ethanol. It is identical with the product prepared in Example 1.

EXAMPLE 3

Preparation of 2-amino-6-methylaminonitrobenzene (Second process)



First step

Preparation of 4-chloro-2-amino-6-methylaminonitrobenzene

First stage

Preparation of 2,4-dichloro-6-methylaminoitrobenzene

0.150 mole (34 g) of 2,4,6-trichloronitrobenzene is added portionwise, at ambient temperature, to 300 ml of a 30% strength solution of methylamine in absolute ethanol. After stirring for 23 hours at ambient temperature, a precipitate, consisting essentially of 4-chloro-2-methylamino-6-methylaminonitrobenzene, is removed by filtration. The filtrate is evaporated to dryness under reduced pressure. 800 ml of concentrated hydrochloric acid are added to the dry extract obtained in this manner. The insoluble fraction is removed by filtration. After dilution of the filtrate with 650 ml of water, the expected product precipitates. It is washed with water and is then dried under vacuum in the presence of phosphorus pentoxide. After recrystallization from isopropanol and then from absolute ethanol, it melts at 120° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_7H_6Cl_2N_2O_2$	Found
C %	38.01	38.02
H %	2.71	2.72
N %	12.67	12.77
O %	14.48	14.40
Cl %	32.13	32.01

Second stage

Preparation of 4-chloro-2-amino-6-methylaminonitrobenzene

0.034 mole (7.5 g) of 2,4-dichloro-6-methylaminonitrobenzene is added in an autoclave to 100 ml of a 28% strength solution of ammonia in water and 50 ml of

ethanol. The reaction mixture is heated to 145°-150° C. for 12 hours, the pressure being 12 kg/cm^2. After cooling, the expected product precipitates from the reaction mixture. After being filtered off and reslurried in water, it is dried hot under vacuum in the presence of phosphorus pentoxide. Recrystallized from isopropanol, it melts at 129° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_7H_8ClN_3O_2$	Found
C %	41.69	41.71
H %	3.97	4.02
N %	20.84	20.80
O %	15.88	15.92
Cl %	17.62	17.49

Second step

Preparation of 2-amino-6-methylaminonitrobenzene

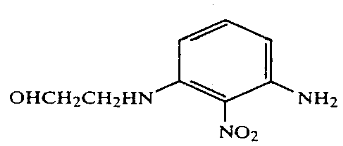
59.5 mg of palladium at a concentration of 10% on charcoal are added to 0.014 mole (2.8 g) of 4-chloro-2-amino-6-methylaminonitrobenzene in 5.3 ml of triethylamine, and 1.16 ml of formic acid are then run in dropwise. A high exothermicity is noted. The reaction mixture is heated to 80° C. for 40 minutes. After dilution of the reaction mixture with ethanol, the catalyst is removed by hot filtration. The filtrate, evaporated under reduced pressure, enables a dry extract to be obtained. After dilution of the dry extract with water, the expected product precipitates. After being filtered off and washed with water, the precipitate is dried under vacuum in the presence of phosphorus pentoxide. After two recrystallizations from isopropanol in order to remove a gum, the product melts at 70° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_7H_9N_3O_2$	Found
C %	50.30	50.19
H %	5.39	5.38
N %	25.15	25.12
O %	19.16	19.42

EXAMPLE 4

Preparation of 2-amino-6-(β-hydroxyethyl)aminonitrobenzene (Third process)



First step

Preparation of β-chloroethyl N-[(3-amino-2-nitro)-phenyl]carbamate

7.5 ml of β-chloroethyl chloroformate are added dropwise over 20 minutes to a mixture of 0.066 mole (10 g) of 2,6-diaminonitrobenzene (reference example) and of 0.036 mole (3.6 g) of calcium carbonate in 50 ml of diethylene glycol dimethyl ether (diglyme) heated to 80° C. Heating is continued for 1 hour after the addition is complete. The reaction mixture is diluted with a mixture of ice and water. The expected product precipitates. When dried hot under vacuum and recrystallized from isopropyl ether and isopropyl alcohol, it melts at 92° C.

Second step

Preparation of N-[(3'-amino-2'-nitro)phenyl]-1, 3-oxazolidin-2-one

3 ml of a 30% strength solution of sodium methylate in methanol are added slowly to a suspension of 0.015 mole (4 g) of the compound prepared in the first step in absolute ethanol. The temperature of the reaction mixture reaches 35° C. The expected product precipitates during the addition. After being reslurried in water and then dried under vacuum in the presence of phosphorus pentoxide, it melts at 132° C.

Third step

Preparation of 2-amino-6-(β-hydroxyethyl) aminonitrobenzene

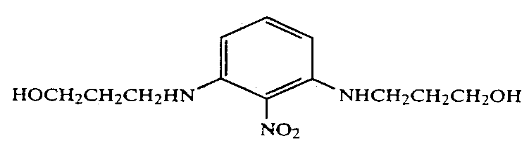
4.5 ml of a 5N sodium hydroxide solution are added dropwise to a solution of 0.011 mole (2.5 g) of the compound prepared in the preceding step in 10 ml of ethanol at 90° C. Heating is continued for one hour. The inorganic salts formed are removed by filtration of the reaction mixture. The aqueous alcoholic filtrate is evaporated to dryness under vacuum. Water is added to the dry residue obtained in this manner; after being acidified, the expected product precipitates. After being filtered off and then dried under vacuum it is recrystallized from isopropyl alcohol. It melts at 129° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{18}N_{11}N_3O_3$	Found
C %	48.72	48.86
H %	5.62	5.45
N %	21.31	21.26
O %	24.34	24.59

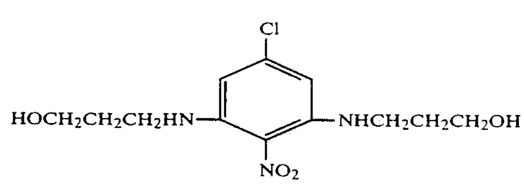
EXAMPLE 5

Preparation of 2-(γ-hydroxypropyl)amino-6-(γ-hy-droxypropyl-)aminonitrobenzene (Second process)



First step

Preparation of 4-chloro-2-(γ-hydroxypropyl)amino-6-(γ-hydroxypropyl)aminonitrobenzene



0.22 mole (50 g) of 2,4,6-trichloronitrobenzene is added portionwise, with stirring, to 150 ml of 3-amino-1-propanol, heated to 80° C. After the end of the addi-

tion, heating is continued for 1 hour 30 minutes. The reaction mixture is poured onto 300 g of iced water. An oil is obtained, which crystallizes after addition of concentrated hydrochloric acid. The precipitate of the expected product is filtered off, and is washed with a 2N solution of hydrochloric acid and then with water to neutrality. After being dried at 40° C. in the presence of phosphorus pentoxide, it is recrystallized from 96° ethanol. It melts at 127° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{12}H_{18}N_3O_4Cl$	Found
C %	47.45	47.41
H %	5.97	6.01
N %	13.83	13.99
O %	21.07	20.98
Cl %	11.67	11.89

Second step

Preparation of 2-(γ-hydroxypropyl)amino-6-(γ-hydroxypropyl)aminonitrobenzene

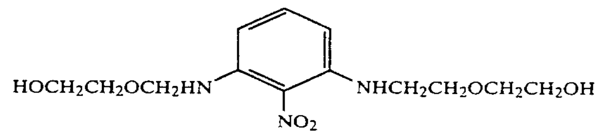
340 mg of palladium at a concentration of 10% on calcium carbonate are added to 0.017 mole (5.2 g) of 4-chloro-2-(γ-hydroxypropyl)amino-6-(γ-hydroxypropyl)amino-nitrobenzene in 11.7 ml of triethylamine. 0.9 ml of acetic acid and 2.3 ml of formic acid are then run in dropwise. A high exothermicity is noted. The reaction mixture is heated under reflux for 3 hours. 10 ml of water are added. The reaction mixture diluted in this manner is filtered hot to remove the catalyst. The expected product precipitates from the filtrate as it cools. It is filtered off, washed with water and then dried under vacuum in the presence of phosphorus pentoxide. Recrystallized from ethyl acetate, it melts at 90° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{12}H_{19}N_3O_4$	Found
C %	53.52	53.60
H %	7.11	7.08
N %	15.60	15.70
O %	23.77	23.71

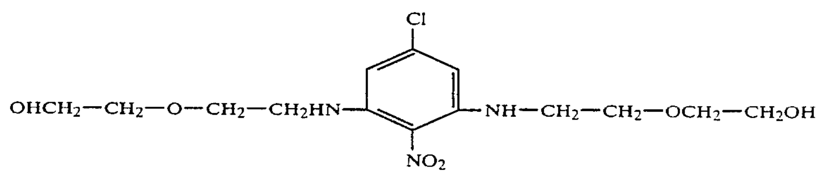
EXAMPLE 6

Preparation of 2-(β-hydroxyethoxyethyl)amino-6-(β-hydroxyethoxyethyl)aminonitrobenzene (Second process)



First step

Preparation of 4-chloro-2(β-hydroxyethoxyethyl)-amino-6-(β-hydroxyethoxyethyl)aminonitrobenzene



A mixture consisting of 0.1 mole (22.6 g) of 2,4, 6-trichloronitrobenzene, 0.6 mole (63 g) of 2-(β-aminoethoxy)ethanol and 20 ml of dioxane is heated under reflux. After 4 hours, the reaction mixture is poured onto 200 g of ice. After being acidified with concentrated hydrochloric acid, the expected product crystallizes out. After filtration, washing with water and drying hot under vacuum, the product is recrystallized from acetonitrile and then from toluene. It melts at 83° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{14}H_{22}N_3O_6Cl$	Found
C %	46.22	45.93
H %	6.10	6.08
N %	11.55	11.79
O %	26.39	26.41
Cl %	9.74	9.81

Second step

Preparation of 2-(β-hydroxyethoxyethyl)amino-6-(β-hydroxyethoxyethyl)aminonitrobenzene

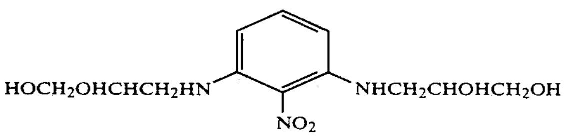
300 mg of palladium at a concentration of 10% on calcium carbonate are added to 0.015 mole (5.45 g) of 4-chloro-2-(β-hydroxyethoxyethyl)amino-6-(β-hydroxyethoxyethyl)aminonitrobenzene in 11 ml of triethylamine. 1.1 ml of acetic acid and 2.05 ml of formic acid are then run in dropwise. When the additions have been completed the reaction mixture is heated under reflux for 30 minutes. 10 ml of water are added. The reaction mixture diluted in this manner is filtered hot to remove the catalyst. The filtrate is evaporated to dryness under vacuum in the presence of absolute ethanol and the residue is taken up with ethyl acetate. Insoluble organic salts are removed by filtration. The ethyl acetate is evaporated off to dryness. Acetonitrile and then water are added to the residue. The expected product precipitates. Recrystallized from ethyl acetate, it melts at 82° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{14}H_{23}N_3O_6$	Found
C %	51.05	51.12
H %	7.04	6.99
N %	12.76	12.99
O %	29.15	28.91

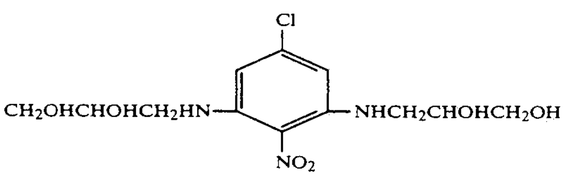
EXAMPLE 7

Preparation of 2-(β,γ-dihydroxypropyl)amino-6-(β,γ-dihydroxypropyl)aminonitrobenzene (Second process)



First step

Preparation of 4-chloro-2-(β,γ-dihydroxypropyl)-amino-6-(β,γ-dihydroxypropyl)aminonitrobenzene



The mixture consisting of 0.1 mole (22.6 g) of 2,4,6-trichloronitrobenzene and 54.7 g of 3-amino-1,2-propanediol in 20 ml of dioxane is heated under reflux. After 4 hours' heating, the dioxane is evaporated off under reduced pressure. The oil obtained is diluted with approximately 300 ml of water. The expected product is obtained by chromatography under pressure, in two operations. Approximately 200 ml of the aqueous solution of the expected product containing 3-amino-1,2-propanediol are injected into a C_{18}RD chromatography column (Waters Prep 500 Apparatus). The expected product is eluted with a solution containing 35% of methanol and 65% of water. After the fractions containing the expected product have been evaporated down, a dry extract is obtained, which is recrystallized from 96° alcohol.

The product obtained melts at 146° C.

Elemental analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{12}H_{18}N_3O_6Cl$	Found
C %	42.92	42.87
H %	5.36	5.37
N %	12.52	12.39
O %	28.61	28.69
Cl %	10.58	10.47

Second step

Preparation of 2-(β,γ-dihydroxypropyl)amino-6-(β,γ-dihydroxypropyl)aminonitrobenzene

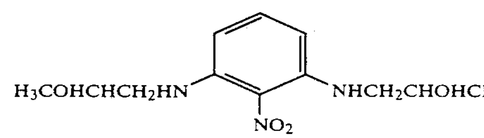
240 mg of palladium at a concentration of 10% on calcium carbonate are added to 0.012 mole (4 g) of 4-chloro-2-(β,γ-dihydroxypropyl)amino-6-(β,γ-dihydroxypropyl)-aminonitrobenzene in 8.6 ml of triethylamine. 0.8 ml of acetic acid and 1.65 ml of formic acid are then added dropwise. The reaction mixture is heated under reflux for 7 hours. 10 ml of water are added. The reaction mixture diluted in this manner is filtered hot to remove the catalyst. The filtrate is evaporated to dryness under vacuum in the presence of absolute ethanol. The residue is dissolved in the minimum quantity of water. The expected product is extracted with ethyl acetate. The ethyl acetate phases are evaporated to dryness, after drying over sodium sulphate. After a small quantity of water has been added to the oil obtained, the expected product precipitates. Recrystallized from ethyl acetate, it melts at 138° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{12}H_{19}N_3O_6$	Found
C %	47.83	47.86
H %	6.36	6.36
N %	13.95	14.13
O %	31.86	31.89

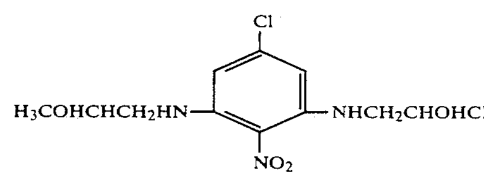
EXAMPLE 8

Preparation of 2-(β-hydroxypropyl)amino-6-(β-hydroxypropyl-)aminonitrobenzene (Second process)



First step

Preparation of 4-chloro-2-(β-hydroxypropyl)amino-6-(β-hydroxypropyl)aminonitrobenzene



0.2 mole (45.3 g) of 2,4,6-trichloronitrobenzene is added in small portions, with stirring, to 180 ml of 3-amino-2-propanol, heated to 80° C. The reaction is exothermic. After 3 hours 30 minutes' heating, the reaction mixture is poured onto 180 ml of iced water. The expected product precipitates. It is filtered off, washed with water to neutrality and then dried under vacuum in the presence of phosphorus pentoxide. After recrystallization from 96° ethanol, it melts at 170° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{12}H_{18}N_3O_4Cl$	Found
C %	47.45	47.40
H %	5.97	5.95
N %	13.83	13.62
O %	21.07	21.12

-continued

Analysis	Calculated for $C_{12}H_{18}N_3O_4Cl$	Found
Cl %	11.67	11.84

Second step

Preparation of 2-(β-hydroxypropyl)amino-6-(β-hydroxypropyl)aminonitrobenzene

340 mg of palladium at a concentration of 10% on active charcoal are added to 0.07 mole (21.3 g) of 4-chloro-2-(β-hydroxypropyl)amino-6-(β-hydroxypropyl)aminonitrobenzene in 30 ml of 96° ethanol and 29.2 ml of triethylamine, after which 5.8 ml of formic acid are run in dropwise.

After the end of the addition, the reaction mixture is heated under reflux for 6 hours. The reaction mixture is filtered hot to remove the catalyst. The filtrate, diluted with 200 ml of water, is extracted with ethyl acetate. After drying over sodium sulphate, followed by evaporation of the ethyl acetate, the gum obtained is purified by chromatography on silica and eluted with a 60/40 mixture of cyclohexane and ethyl acetate.

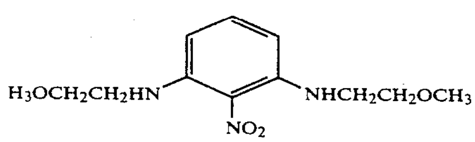
The product obtained melts at 73° C.

Elemental analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{12}H_{19}N_3O_4$	Found
C %	53.52	53.53
H %	7.11	7.10
N %	15.60	15.53
O %	23.76	23.67

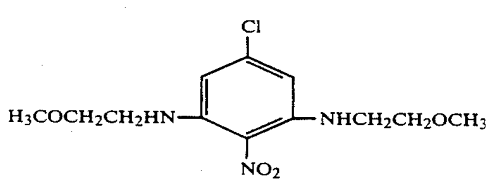
EXAMPLE 9

Preparation of 2-(β-methoxyethyl)amino-6-(β-methoxyethyl)aminonitrobenzene (Second process)



First step

Preparation of 4-chloro-2-(β-methoxyethyl)amino-6-(β-methoxyethyl)aminonitrobenzene



0.2 mole (45.3 g) of 2,4,6-trichloronitrobenzene is added portionwise, with stirring, to 180 ml of 2-methoxyethylamine, heated to 80° C. After the end of the addition the heating is continued for 2 hours 30 minutes. The reaction mixture is diluted with 180 ml of iced water. The expected product precipitates. It is filtered off, washed with water and dried under vacuum at 60° C. in the presence of phosphorus pentoxide. Recrystallized from 96° ethanol, it melts at 90° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated from $C_{12}H_{18}N_3O_4Cl$	Found
C %	47.45	47.49
H %	5.97	6.01
N %	13.83	13.92
O %	21.07	20.91
Cl %	11.67	11.49

Second step

Preparation of 2-(β-methoxyethyl)amino-6-(β-methoxyethyl)aminonitrobenzene

0.4 g of palladium at a concentration of 10% on active charcoal is added to 0.084 mole (25.5 g) of 4-chloro-2-(β-methoxyethyl)amino-6-(β-methoxyethyl)aminonitrobenzene in 33.4 ml of triethylamine, after which 7 ml of formic acid are added dropwise. At the end of the additions, the reaction mixture is heated for 1 hour 30 minutes, under reflux. The reaction mixture is diluted with 100 ml of 96° alcohol and 100 ml of water. The expected product precipitates. After filtration, the expected product containing the catalyst is dissolved in 90 ml of isopropyl alcohol. The catalyst is removed by hot filtration. The expected product crystallizes.

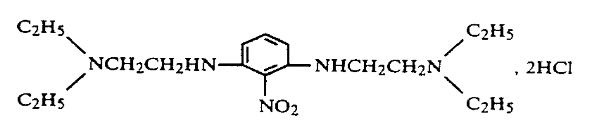
It is purified by a preparative chromatography on a C_{18} column (Waters Prep 500 apparatus) and eluted with a mixture of water (40%) and methanol (60%). It melts at 56° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{12}H_{19}N_3)_4$	Found
C %	53.52	63.42
H %	7.11	7.10
N %	15.60	15.60
O %	23.77	23.69

EXAMPLE 10

Preparation of 2-(β-diethylaminoethyl)amino-6-(β-diethylaminoethyl)aminonitrobenzene dihydrochloride (Second process)



1st step

Preparation of 4-chloro-2-(β-diethylaminoethyl)amino-6-(β-diethylaminoethyl)aminonitrobenzene

0.2 mole (45.3 g) of 2,4,6-trichloronitrobenzene is added portionwise, with stirring, to 180 ml of N,N-diethylethylenediamine, heated to 60° C. After the end of the addition, heating is continued for 30 minutes. The reaction mixture is diluted with 180 ml of iced water. The expected product precipitates. It is filtered off, washed with water and then dried under vacuum at 60° C. in the presence of phosphorus pentoxide. After recrystallization from 96° ethanol, it melts at 90° C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{18}H_{32}N_5O_2Cl$	Found
C %	56.02	56.02
H %	8.36	8.30
N %	18.15	17.96
O %	8.29	8.46
Cl %	9.19	9.05

Second step

Preparation of 2-(β-diethylaminoethyl)amino-6-(β-diethylaminoethyl)aminonitrobenzene dihydrochloride

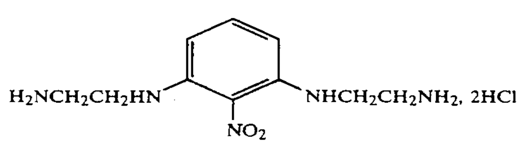
300 mg of palladium at a concentration of 10% on calcium carbonate are added to 0.015 mole (5.8 g) of 4-chloro-2-(β-diethylaminoethyl)amino-6-(β-diethylaminoethyl)aminonitrobenzene in 11.1 ml of triethylamine, after which 2.86 ml of acetic acid and 2.1 ml of formic acid are added dropwise. After the end of the additions, the materials are heated under reflux for 3 hours 30 minutes. The reaction mixture is diluted with 10 ml of water. The catalyst is removed by hot filtration. The filtrate is evaporated to dryness under vacuum. The inorganic salts are precipitated by adding acetone and are removed by filtration. After evaporation of the acetone, an oil is obtained and this, after treatment with a solution of hydrochloric acid in absolute ethanol, leads to the expected product which is isolated by evaporating off the alcohol and precipitating with ethyl ether.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{18}H_{35}Cl_2N_5O_2$	Found
C %	50.94	50.79
H %	8.25	8.30
N %	16.51	16.59
O %	7.55	7.69
Cl %	16.74	16.71

EXAMPLE 11

Preparation of 2-(β-aminoethyl)amino-6-(β-aminoethyl)aminonitrobenzene dihydrochloride (First process)



0.16 mole (30 g) of 2,6-dichloronitrobenzene is added to 100 ml of ethylenediamine. The mixture is heated under reflux for 4 hours. The unreacted ethylene diamine is stripped off under vacuum. The expected product is precipitated by adding a 7N solution of hydrochloric acid to the residue obtained.

The product is dissolved in 50 ml of water. After having been filtered to remove an insoluble material, the solution is made alkaline with sodium hydroxide and is extracted with ethyl acetate.

The combined ethyl acetate phases are dried over sodium sulphate. After evaporation of the ethyl acetate under vacuum a residue is obtained. The expected product is precipitated by adding a 7N solution of hydrochloric acid in absolute ethanol.

Analysis of the purified product gives the following results:

Analysis	Calculated for $C_{10}H_{19}Cl_2N_5O_2$	Found
C %	38.46	38.50
H %	6.09	6.10
N %	22.43	22.53
O %	10.25	10.41
Cl %	22.76	22.76

APPLICATION EXAMPLE 1

The following dyeing mixture is prepared:

2,6-Diaminonitrobenzene	0.1 g
2-Butoxyethanol	10 g
Cellosize W.P. 03 - Union Carbide Company (hydroxyethylcellulose)	2 g
Cetyldimethylhydroxyethylammonium chloride	2 g
5% strength aqueous ammonia	0.9 g
Water q.s.	100 g
pH: 10	

This mixture, applied to bleached hair for 30 minutes at 28° C. imparts a light salmon color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 2

The following dyeing mixture is prepared:

2-(β-hydroxyethyl)amino-6-(β-hydroxyethyl)-aminonitrobenzene	0.1 g
2-Butoxyethanol	10 g
Cellosize W.P. 03 Union Carbide Company (hydroxyethylcellulose)	2 g
Ammonium lauryl sulphate	5 g
5% strength aqueous ammonia	0.9 g
Water q.s.	100 g
pH: 9	

This mixture, applied to 90% naturally white hair for 30 minutes at 28° C. imparts a silvery light pink color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 3

The following dyeing mixture is prepared:

2-Amino-6-methylaminonitrobenzene	0.25 g
2-Butoxyethanol	5 g
Propylene glycol	5 g
Alfol C 16/18 - Condea Company	8 g
(cetylstearyl alcohol)	8 g
Lanette Wax E - Henkel Company	0.5 g
(sodium cetylstearyl sulphate)	0.5 g
Cémulsol B - Rhône-Poulenc Company (ethoxylated castor oil)	1 g
Oleoyldiethanolamide	1.5 g
Water q.s.	100 g
pH: 7.3	

This mixture, applied to bleached hair for 20 minutes at 27° C, imparts a purplish-blue-pink color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 4 I

Oxidation dye

The following dyeing mixture is prepared:

2,6-Diaminonitrobenzene	0.3 g
p-Aminophenol	0.05 g
Resorcin	0.08 g
4-Amino-3-hydroxytoluene	0.08 g
(N,N-di-β-hydroxyethyl)aminoaniline sulphate	0.19 g
96° ethanol	10 g
Cémulsol NP 4 - Rhône-Poulenc (nonylphenol oxyethylenated with 4 moles of ethylene oxide)	12 g
Cémulsol NP 9 - Rhône-Poulenc (nonylphenol oxyethylenated with 9 moles of ethylene oxide)	15 g
Oleyl alcohol polyglycerolated with 2 moles of glycerol	1.5 g
Oleyl alcohol polyglycerolated with 4 moles of glycerol	1.5 g
Propylene glycol	6 g
Trilon B (ethylenediaminetetraacetic acid)	0.12 g
22° Bé aqueous ammonia	11 g
Thioglycolic acid	0.6 g
Water q.s.	100 g
pH: 10.6	

120 g of 20-volume hydrogen peroxide are added at the time of use. The mixture, applied to natural grey hair for 20 minutes at 27° C, imparts an ashen, very light chestnut-brown color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 5

The following dyeing mixture is prepared:

2,6-Diaminonitrobenzene	0.25 g
3-Nitro-4-N'-(β-hydroxyethyl)amino-N,N-(di-β-hydroxyethyl)aniline	0.45 g
(3-Methylamino-4-nitro)phenoxy ethanol	0.25 g
2-Butoxy ethanol	10 g
Cémulsol NP 4 - Rhône-Poulenc Company (nonylphenol with 4 moles of ethylene oxide)	12 g
Cémulsol NP 9 - Rhône-Poulenc Company (nonylphenol with 9 moles of ethylene oxide)	15 g
Oleyl alcohol polyglycerolated with 2 moles of glycerol	1.5 g
Oleyl alcohol polyglycerolated with 4 moles of glycerol	1.5 g
Monoethanolamine as 20% strength by weight aqueous solution	2 g
Water q.s.	100 g
pH: 9.5	

This mixture, applied to natural grey hair for 20 minutes at 30° C, imparts an ash-blonde color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 6

The following dyeing mixture is prepared:

2-(β-Hydroxyethyl)amino-6-(β-hydroxyethyl)-aminonitrobenzene	0.25 g
3-Nitro-4-N'-(γ-hydroxypropyl)amino-N,N-(di-β-hydroxyethyl)aniline	0.30 g
(3-Methylamino-4-nitro)phenyl β,γ-dihydroxypropyl ether	0.2 g
Carbopol 934 - Goodrich Chemicals Company (polyacrylic acid crosslinked with a polyfunctional agent)	2 g
Ethanol	10 g
Triethanolamine	5 g
Water q.s.	100 g
pH: 7.5	

This mixture, applied to bleached hair for 25 minutes at 27° C, imparts a pink-marron glace color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 7

The following dyeing mixture is prepared:

2-Amino-6-methylaminonitrobenzene	0.1 g
2,6-Diamino-4-chloronitrobenzene	0.4 g
2-(β-hydroxyethyl)amino-4-(β-hydroxyethyl)-amino-5-chloronitrobenzene	0.2 g
1,4,5,8-Tetraaminoanthraquinone	0.14 g
Ethanol	15 g
Cémulsol NP 4-Rhône-Poulenc Company (nonylphenol with 4 moles of ethylene oxide)	12 g
Cémulsol NP 9-Rhône-Poulenc Company (nonylphenol with 9 moles of ethylene oxide)	15 g
Oleyl alcohol polyglycerolated with 2 moles of glycerol	1.5 g
Oleyl alcohol polyglycerolated with 4 moles of glycerol	1.5 g
1% strength aqueous triethanolamine	1.3 g
Water q.s.	100 g
pH: 9	

This mixture, applied to bleached hair for 25 minutes at 30° C., imparts a golden blonde color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 8

Oxidation dye

The following dyeing mixture is prepared:

2,6-Diaminonitrobenzene	1 g
para-Phenylenediamine	0.1 g
para-Aminophenol	0.07 g
meta-Aminophenol	0.12 g
(2,4-Diamino)phenoxyethanol dihydrochloride	0.06 g
4-N-methylaminophenol hemisulphate	0.12 g
Alfol C 16/18-Condea Company (cetylstearyl alcohol)	8 g
Lanette Wax E-Henkel Company (sodium cetylstearylsulphate)	0.5 g
Cémulsol B-Rhône-Poulenc (ethoxylated castor oil)	1 g
Oleyldiethanolamine	1.5 g
Masquol DTPA-Protex Company (pentasodium diethylenetriaminepentaacetate)	2 5 g
22° Bé aqueous ammonia	11 g
Water q.s.	100 g
pH 10.2	

100 g of 20-volume hydrogen peroxide are added at the time of use. The mixture, applied to 90% naturally white hair for 25 minutes at 38° C., imparts a coppery, medium chestnut-brown color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 9

Oxidation dye

The following dyeing mixture is prepared:

2-(β-Hydroxyethyl)amino-6-(β-hydroxyethyl)-aminonitrobenzene	0.6 g
para-Phenylene diamine	0.06 g
para-Aminophenol	0.5 g
meta-Aminophenol	0.4 g
Resorcin	0.4 g
4-(β-Hydroxyethyl)amino-2-hydroxytoluene	0.1 g
Cémulsol NP4-Rhône-Poulenc Company (nonylphenol with 4 moles of ethylene oxide)	21 g
Cémulsol NP9-Rhône-Poulenc Company (nonylphenol with 9 moles of ethylene oxide)	24 g

-continued

Oleic acid	4 g
Butylglycol	3 g
96° ethanol	10 g
Masquol DTPA-Protex (pentasodium diethylenetriaminepentaacetate)	2.5 g
35° Bé Socium hydrogen sulphite solution	1 g
Aqueous ammonia	10 g
Water q.s.	100 g
pH: 10.5	

100 g of 20-volume hydrogen peroxide are added at the time of use. The mixture, applied to 90% naturally white hair for 20 minutes at 38° C., imparts a coppery light chestnut-brown color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 10

The following dyeing mixture is prepared:

2-Amino-6-(β-hydroxyethyl)aminonitrobenzene	0.5 g
2-Butoxyethanol	15 g
Cellosize W.P. 03-Union Carbide Company (hydroxyethylcellulose)	2 g
Cetyldimethylhydroxyethylammonium chloride	2 g
Water q.s.	100 g
pH: 11	

This mixture, applied to natural grey hair for 30 minutes at 30° C., imparts a light red color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 11

The following dyeing mixture is prepared:

2-(β-Hydroxypropyl)amino-6-(γ-hydroxypropyl)-aminonitrobenzene	0.25 g
96° alcohol	9 g
Carbopol 934-Goodrich Chemicals Company (crosslinked polyacrylic acid)	2 g
Triethanolamine	3 g
Water q.s.	100 g
pH: 8.3	

This mixture, applied to 90% naturally white hair for 25 minutes at 35° C., imparts a slightly grey red color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 12

The following dyeing mixture is prepared:

2-(β-Hydroxypropyl)amino-6-(β-hydroxypropyl)-aminonitrobenzene	0.26 g
2-Butoxyethanol	10 g
Alfol C 16/18-Condea Company (cetylstearyl alcohol)	8 g
Lanette Wax E-Henkel Company (sodium cetylstearyl sulphate)	0.5 g
Cémulsol B-Rhône-Poulenc Company (ethoxylated castor oil)	1 g
Oleoyldiethanolamide	1.5 g
Triethanolamine	4 g
Water q.s.	100 g
pH: 9.4	

This mixture, applied to bleached hair for 25 minutes at 35° C., imparts a grey purple-red color it, after shampooing and rinsing.

APPLICATION EXAMPLE 13

The following dyeing mixture is prepared:

2-(β,γ-Dihydroxypropyl)amino-6-(β,γ-dihydroxypropyl)aminonitrobenzene	0.238 g
Propylene glycol	12 g
Cellosize W.P. 03-Union Carbide Company (hydroxyethylcellulose)	2 g
Cetyldimethylhydroxyethylammonium chloride	2 g
20% strength aqueous ammonia solution	3 g
Water q.s.	100 g
pH: 10.4	

This mixture, applied to permanent-waved hair for 30 minutes at 35° C. imparts a slightly grey red color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 14

The following dyeing mixture is prepared:

2-(β-Methoxyethyl)amino-6-(β-methoxyethyl)-aminonitrobenzene	0.105 g
Propylene glycol	10 g
Alfol C 16/18-Condea Company (cetylstearyl alcohol)	8 g
Lanette Wax E-Henkel Company (sodium cetylstearylsulphate)	0.5 g
Cémulsol B-Rhône-Poulenc Company (ethoxylated castor oil)	1 g
Oleoyldiethanolamide	1.5 g
20% strength aqueous ammonia solution	2 g
Water q.s.	100 g
pH: 10	

This mixture, applied to permanent-waved hair for 25 minutes at 35° C., imparts a slightly grey, light red-brown color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 15

The following dyeing mixture is prepared:

2-(β-Diethylaminoethyl)amino-6-(β-diethyl-aminoethyl)aminonitrobenzene	0.17 g
Propylene glycol	10 g
Alfol C 16/18-Condea Company (cetylstearyl alcohol)	8 g
Lanette Wax E-Henkel Company (sodium cetylstearylsulphate)	0.5 g
Cémulsol B-Rhône-Poulenc Company (ethoxylated castor oil)	1 g
Oleoyldiethanolamide	1.5 g
20% strength aqueous ammonia solution	5 g
Water q.s.	100 g
pH: 10	

This mixture, applied to bleached hair for 35 minutes at 35° C., imparts a light yellow-brown color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 16

The following dyeing mixture is prepared:

2-(β-Hydroxyethoxyethyl)amino-6-(β-hydroxy-ethoxyethyl)aminonitrobenzene	0.10 g
2-Butoxyethanol	11 g
Cellosize W.P. 03-Union Carbide Company (hydroxyethylcellulose)	2 g
Cetyldimethylhydroxyethylammonium chloride	2 g
Monoethanolamine	6 g
Water q.s.	100 g

-continued

pH: 10	

This mixture, applied to permanent-waved hair for 25 minutes at 35° C., imparts a light grey red-brown color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 17

Oxidation dye

The following dyeing mixture is prepared:

2-(γ-Hydroxypropyl)amino-6-(γ-hydroxypropyl)-aminonitrobenzene	1.5 g
para-Phenylenediamine	0.1 g
para-Aminophenol	0.07 g
meta-Aminophenol	0.14 g
(2,4-Diamino)phenoxyethanol dihydrochloride	0.06 g
4-N-methylaminophenol hemisulphate	0.13 g
Alfol C 16/18-Condea Company (cetylstearyl alcohol)	8 g
Lanette Wax E-Henkel Company (sodium cetylstearylsulphate)	0.5 g
Cémulsol B-Rhône-Poulenc (ethoxylated castor oil)	1 g
Oleoyldiethanolamide	1.5 g
Masquol DTPA-Protex Company (pentasodium diethylenetriaminepentaacetate)	2.5 g
22° Bé aqueous ammonia	11 g
Water q.s.	100 g
pH: 10	

100 g of 20-volume hydrogen peroxide are added at the time of use. The mixture, applied to 90% white hair for 25 minutes at 38° C., imparts a purple-violet light chestnut-brown color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 18

Oxidation dye

The following dyeing mixture is prepared:

2-Amino-6-(β-hydroxyethyl)aminonitrobenzene	0.6 g
para-Phenylenediamine	0.06 g
para-Aminophenol	0.5 g
meta-Aminophenol	0.4 g
Resorcin	0.4 g
4-(β-hydroxyethyl)amino-2-hydroxytoluene	0.1 g
Cémulsol NP4-Rhône-Poulenc (nonylphenol with 4 moles of ethylene oxide)	21 g
Cémulsol NP9-Rhône-Poulenc (nonylphenol with 9 moles of ethylene oxide)	24 g
Oleic acid	4 g
2-butoxyethanol	3 g
96° ethanol	10 g
Masquol DTPA-Protex (pentasodium diethylenetriaminepentaacetate)	2.5 g
35° Bé sodium bisulphite solution	1 g
Aqueous ammonia	10 g
Water q.s.	100 g
pH: 10.3	

100 g of 20-volume hydrogen peroxide are added at the time of use. The mixture, applied to 90% naturally white hair for 20 minutes at 38° C., imparts a coppery, very light chestnut-brown color to it, after shampooing and rinsing.

APPLICATION EXAMPLE 19

Oxidation dye

The following dyeing mixture is prepared:

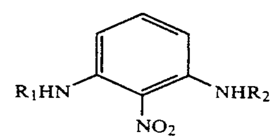
2-(β,γ-dihydroxypropyl)amino-6-(β,γ-dihydroxypropyl)aminonitrobenzene	0.5 g
p-Aminophenol	0.05 g
Resorcin	0.08 g
4-Amino-2-hydroxytoluene	0.08 g
(N,N-di-β-hydroxyethyl)aminoaniline sulphate	0.19 g
96° ethanol	10 g
Cemulsol NP 4-Rhone-Poulenc (nonylphenol-oxyethylenated with 4 moles of ethylene oxide)	12 g
Cemulsol NP 9-Rhone-Poulenc (nonylphenol-oxyethylenated with 9 moles of ethylene oxide)	15 g
Oleyl alcohol polyglycerolated with 2 moles of glycerol	1.5 g
Oleyl alcohol polyglycerolated with 4 moles of glycerol	1.5 g
Propylene glycol	6 g
Trilon B (ethylenediaminetetraacetic acid)	0.12 g
22° Be aqueous ammonia	11 g
Thioglycolic acid	0.6 g
Water q.s.	100 g
pH: 10.6	

120 g of 20-volume hydrogen peroxide are added at the time of use. The mixture, applied to 90% white hair for 20 minutes at 27° C., imparts a coppery, light blonde color to it, after shampooing and rinsing.

We claim:

1. A process for preparing a compound having the formula

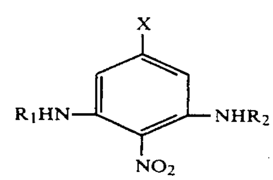
(I)



wherein

R_1 and R_2, each independently, represent hydrogen, alkyl containing 1–6 carbon atoms, monohydroxyalkyl containing 1–6 carbon atoms, polyhydroxyalkyl containing 1–6 carbon atoms, alkoxyalkyl wherein the alkyl moiety contains 1–6 carbon atoms, hydroxyalkoxyalkyl wherein the alkyl moiety contains 1–6 carbon atoms or aminoalkyl wherein the alkyl moiety contains 1–6 carbon atoms and wherein the amino moiety is unsubstituted or substituted with 1–2 alkyl or hydroxyalkyl groups wherein said alkyl has 1–6 carbon atoms or wherein the nitrogen atom of said aminoalkyl forms part of a heterocycle, said process comprising dehalogenating a compound of the formula

(II)

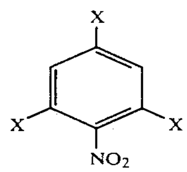


wherein X halogen and R_1 and R_2 have the meanings given above, with triethylamine formate in the presence of palladium on a support without involving the simultaneous reduction of the nitro group, said support being selected from the group consisting of barium sulfate, barium carbonate, alumina and calcium carbonate.

2. The process of claim 1 wherein a solvent is present.

3. The process of claim 2 wherein said solvent is an alcohol, dimethylformamide, N-methylpyrrolidone or acetic acid.

4. The process of claim 1 wherein the compound of formula II, wherein R_1 and R_2 are identical and are other than hydrogen, is prepared by reacting a 2,4,6-trihalonitrobenzene having the formula

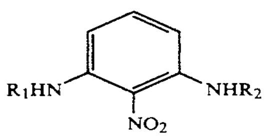


wherein X is halogen with an amine having the formula NH_2R_1 wherein R_1 has the meaning given in claim **34** with the proviso that R_1 is not hydrogen at a temperature ranging from 10° C. to the reflux temperature of the amine of formula NH_2R_1 or of any solvent present.

5. The process of claim 4 carried out in an autoclave at a maximum pressure of 25 kg/cm^2 when said amine of formula NH_2R_1 has a boiling temperature lower than or equal to ambient temperature.

6. A process for preparing a 2-nitro metaphenylenediamine compoud having the formula

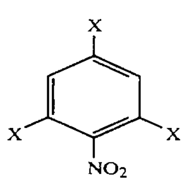
(I)



wherein

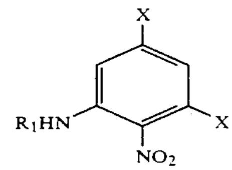
R_1 and R_2 are different and each, independently, represent hydrogen, alkyl containing 1–6 carbon atoms, monohydroxyalkyl containing 1–6 carbon atoms, polyhydroxyalkyl containing 1–6 carbon atoms, alkoxyalkyl wherein the alkyl moiety contains 1–6 carbon atoms, hydroxyalkoxyalkyl wherein the alkyl moiety contains 1–6 carbon atoms, or aminoalkyl wherein the alkyl moiety contains 1–6 carbon atoms and wherein the amino moiety is unsubstituted or substituted with 1–2 alkyl or hydroxyalkyl groups wherein said alkyl has 1–6 carbon atoms or wherein the nitrogen atom of said aminoalkyl forms part of a heterocycle, said process comprising, in a first step, reacting a 2,4,6-trihalonitrobenzene having the formula

(VI)



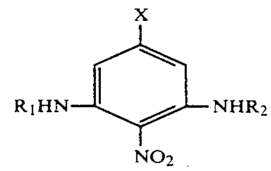
wherein X is halogen with ammonia or an amine of the formula NH_2R_1 wherein R_1 has the meaning given above to produce a compound having the formula

(V)



in a second step, reacting said compound having formula (V) with ammonia or an amine of the formula NH_2R_2 wherein R_2 has the meaning given above, the reaction in both said first and second steps being carried out at a temperature ranging from 10° C. to the reflux temperature of the ammonia or amine present or of any solvent present to produce a compound having the formula

(II)

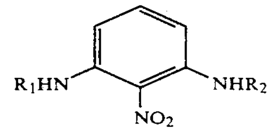


wherein R_1 and R_2 have the meaning given above and X is halogen, and

in a third step, dehalogenating said compound having formula (II) with triethylamine formate in the presence of palladium on a support, said support being selected from the group consisting of barium sulfate, barium carbonate, alumina and calcium carbonate.

7. A process for preparing a compound having the formula

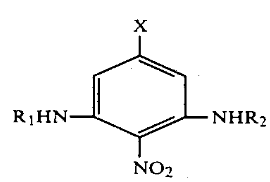
(I)



wherein

R_1 and R_2, each independently, represent hydrogen, alkyl containing 1–6 carbon atoms, monohydroxyalkyl containing 1–6 carbon atoms, polyhydroxyalkyl containing 1–6 carbon atoms, alkoxyalkyl wherein the alkyl moiety contains 1–6 carbon atoms, hydroxyalkoxyalkyl wherein the alkyl moiety contains 1–6 carbon atoms, or aminoalkyl wherein the alkyl moiety contains 1–6 carbon atoms and wherein the amino moiety is unsubstituted or substituted with 1–2 alkyl or hydroxyalkyl groups wherein said alkyl has 1–6 carbon atoms or wherein the nitrogen atom of said aminoalkyl forms part of a heterocycle, said process comprising dehalogenating a compound of the formula

(II)



wherein X is halogen and R_1 and R_2 have the meanings given above with triethylamine formate, the dehalogenation reaction being carried out with palladium on calcium carbonate or palladium on barium carbonate without involving the simultaneous reduction of the nitro group, in the presence of acetic acid, formic acid and triethylamine.

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